Claims

What is claimed:

1. A reaction system for the preparation of a fiber reinforced composite according to the pultrusion process comprising:
    a. a reaction mixture comprising an isocyanate reactive composition, a polyisocyanate composition, and optionally one or more additives; and
    b. a continuous fiber reinforcing material,

    wherein the reaction mixture initially contains both free isocyanate groups and free alcoholic –OH groups, has a gel time greater than 768 seconds at 25°C, and a gel time less than 120 seconds at 175°C.

2. The reaction system according to claim 1, wherein the reaction system is a mixing activated thermosetting system that cures by forming a covalently crosslinked network structure.

3. The reaction system according to claim 2, wherein the reaction system is substantially free of organic species with boiling points below 180°C at 760 mmHg pressure.

4. The reaction system according to claim 3, wherein the reaction system is essentially free of water.

5. The reaction system according to claim 1, wherein the polyisocyanate composition comprises one or more polyisocyanates of the MDI series, has a number averaged functionality of isocyanate groups in the range of from 2.3 to 2.9, and a free isocyanate group content in the range of from 10% by weight to 33.6% by weight.

6. The reaction system according to claim 1, wherein the isocyanate reactive composition comprises a mixture of (i) from greater than 0 up to 20% by weight of at least one polyol having a number averaged molecular weight of 1500 or greater and a number averaged functionality of 2 to 4, (ii) 60 to 100% weight of at least one polyol having a number

averaged molecular weight between 250 and 750 and a number averaged functionality of 3 to 4, and (iii) 2 to about 30% by weight of at least one polyol having a number averaged functionality of 2 to 3 and a number averaged molecular weight of less than 200; wherein the weights of (i) + (ii) + (iii) total 100% of the isocyanate reactive composition.

7. The reaction system according to claim 1, wherein the isocyanate reactive composition comprises a mixture of (I) 60 to 100% weight of at least one polyol having a number averaged molecular weight between 250 and 750 and a number averaged functionality of 3 to 4, and (II) 2 to about 30% by weight of a least one polyol having a number averaged functionality of 2 to 3 and a number averaged molecular weight of less than 200; wherein the weights of (I) + (II) total 100% of the isocyanate reactive composition.

8. The reaction system according to claim 1, wherein the isocyanate reactive composition comprises a total of at least 10% by weight, relative to the total weight of the isocyanate reactive composition, of at least one hydrophobic polyol selected from the group consisting of hydrocarbon backbone polyols of number averaged molecular weight greater than 500, fatty ester polyols of number averaged molecular weight greater than 500, and fatty polyester polyols of number averaged molecular weight greater than 500.

9. The reaction system according to claim 8, wherein the at least one hydrophobic polyol is a fatty polyester polyol having a number averaged functionality of organically bound isocyanate-reactive hydroxyl groups of greater than 2.

10. The reaction system according to claim 9, wherein the additive comprises an organobismuth catalyst, an organozinc catalysts, or mixtures thereof.

11. The reaction system according to claim 9, wherein the additive comprises at least one organobismuth catalyst and at least one organozinc catalyst.

12. The reaction system according to claim 9, wherein the fatty polyester polyol is castor oil.

13. The reaction system according to claim 1, wherein the isocyanate reactive composition comprises castor oil and at least one other polyol.

14. The reaction system according to claim 1, wherein the additive comprises an organobismuth catalyst, an organozinc catalysts, or mixtures thereof.

15. The reaction system according to claim 1, wherein the additive comprises at least one organobismuth catalyst and at least one organozinc catalyst.

16. The reaction system according to claim 14, wherein the isocyanate reactive composition comprises a total of at least 10% by weight, relative to the total weight of the isocyanate reactive composition, of at least one hydrophobic polyol selected from the group consisting of hydrocarbon backbone polyols of number averaged molecular weight greater than 500, fatty ester polyols of number averaged molecular weight greater than 500, and fatty polyester polyols of number averaged molecular weight greater than 500.

17. The reaction system according to claim 15, wherein the isocyanate reactive composition comprises a total of at least 10% by weight, relative to the total weight of the isocyanate reactive composition, of at least one hydrophobic polyol selected from the group consisting of hydrocarbon backbone polyols of number averaged molecular weight greater than 500, fatty ester polyols of number averaged molecular weight greater than 500, and fatty polyester polyols of number averaged molecular weight greater than 500.

18. The reaction system according to claim 1, wherein the polyisocyanate composition comprises a total of at least 5% by weight, relative to the total weight of the polyisocyanate composition, of at least one isocyanate terminated prepolymer formed from a hydrophobic polyol selected from the group consisting of hydrocarbon backbone polyols of number averaged molecular weight greater than 500, fatty ester polyols of number averaged molecular weight greater than 500, and fatty polyester polyols of number averaged molecular weight greater than 500.

19. The reaction system according to claim 1, wherein the polyisocyanate composition comprises an isocyanate terminated prepolymer formed from a fatty polyester polyol having a number averaged functionality of organically bound isocyanate-reactive hydroxyl groups of greater than 2.

20. The reaction system according to claim 1, wherein the polyisocyanate composition comprises an isocyanate terminated prepolymer formed from castor oil.

21. A pultrusion process for preparing a fiber reinforced composite comprising the steps of:
    (a) pulling continuous fibers through an impregnation die while contacting the fibers with a reaction mixture comprising an isocyanate reactive composition, a polyisocyanate composition, and optionally one or more additives, sufficient to cause substantial polymerization of the reaction mixture within the impregnation die to produce a composite of fibers coated by the reaction mixture, which is not fully cured,
    (b) directing the composite of fibers coated by the reaction mixture through a heated curing die to further advance the cure of the reaction mixture so as to produce a solid fiber reinforced composite, and
    (c) withdrawing the solid fiber reinforced composite from the curing die;
    wherein the reaction mixture initially contains both free alcoholic –OH groups and free isocyanate (-NCO) groups, has a gel time of greater than 768 seconds at 25°C, and a gel time of less than 120 sec at 175°C.

22. The process according to claim 21, wherein the additive comprises a catalytically effective amount of at least one catalyst selected from the group consisting of organobismuth catalysts and organozinc catalysts.

23. The process according to claim 21, wherein the additive comprises a catalytically effective amount of at least one organobismuth catalyst and at least one organozinc catalyst.

24. The process according to claim 21, wherein the reaction mixture contains at least one hydrophobic polyol selected from the group consisting of hydrocarbon backbone polyols of number averaged molecular weight greater than 500, fatty ester polyols of number averaged molecular weight greater than 500, and fatty polyester polyols of number averaged molecular weight greater than 500.

25. The process according to claim 24, wherein the hydrophobic polyol is a fatty polyester polyol having a number averaged functionality of organically bound isocyanate-reactive hydroxyl groups of greater than 2.

26. The process according to claim 24, wherein the hydrophobic polyol is castor oil.

27. The process according to claim 21, wherein the polyisocyanate composition contains at least one isocyanate terminated prepolymer derived from a hydrophobic polyol selected from the group consisting of hydrocarbon backbone polyols of number averaged molecular weight greater than 500, fatty ester polyols of number averaged molecular weight greater than 500, and fatty polyester polyols of number averaged molecular weight greater than 500.

28. The process according to claim 27 wherein the hydrophobic polyol is a fatty polyester polyol having a number averaged functionality of organically bound isocyanate-reactive hydroxyl groups of greater than 2.

29. The process according to claim 28, wherein the hydrophobic polyol is castor oil.

30. The process according to claim 21, wherein the polyisocyanate composition comprises one or more polyisocyanates of the MDI series, has a number averaged functionality of isocyanate groups in the range of from 2.3 to 2.9, and a free isocyanate group content in the range of from 10% by weight to 33.6% by weight.

31. The process according to claim 21, wherein the isocyanate reactive composition comprises a mixture of (i) from greater than 0 up to 20% by weight of at least one polyol having a

number averaged molecular weight of 1500 or greater and a number averaged functionality of 2 to 4, (ii) 60 to 100% weight of at least one polyol having a number averaged molecular weight between 250 and 750 and a number averaged functionality of 3 to 4, and (iii) 2 to about 30% by weight of a least one polyol having a number averaged functionality of 2 to 3 and a number averaged molecular weight of less than 200; wherein the weights of (i) + (ii) + (iii) total 100% of said isocyanate reactive composition.

32. The process according to claim 21, wherein the isocyanate reactive composition comprises a mixture of (I) 60 to 100% weight of at least one polyol having a number averaged molecular weight between 250 and 750 and a number averaged functionality of 3 to 4, and (II) 2 to about 30% by weight of a least one polyol having a number averaged functionality of 2 to 3 and a number averaged molecular weight of less than 200; wherein the weights of (I) + (II) total 100% of said isocyanate reactive composition.

33. A fiber reinforced composite prepared according to the process of claim 21.

34. A fiber reinforced composite prepared from the reaction system of claim 1.